

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08L 67/02, 77/00, 75/04, 23/06, 23/08, 71/00	A1	(11) International Publication Number: WO 95/16746 (43) International Publication Date: 22 June 1995 (22.06.95)
(21) International Application Number: PCT/US94/14365 (22) International Filing Date: 13 December 1994 (13.12.94) (30) Priority Data: 93120042.2 13 December 1993 (13.12.93) EP (34) Countries for which the regional or international application was filed: AT et al. (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): CARDINAL, Jean-Claude [FR/CH]; 3, route de Courte-Raye, CH-1297 Founex (CH). HAUSMANN, Karl-Heinz [DE/CH]; Sablons 57, CH-2000 Neuchâtel (CH). (74) Agents: KAEDING, Konrad, S. et al.; E.I. Du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: BREATHABLE FILM (57) Abstract A thermoplastic composition containing a mixture of (a) a block copolyether ester, a block copolyether amide and/or a polyurethane; (b) a thermoplastic homo-, co- or terpolymer that is incompatible with (a); and (c) a compatibilizer; and its use in preparing films is disclosed. Such films demonstrate moisture vapor permeability, while acting as barriers to liquids and microorganisms.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

BREATHABLE FILM

- This invention relates to a thermoplastic composition and its use in preparing films demonstrating moisture vapor, oxygen and carbon dioxide permeability, while acting as barriers to liquids and microorganisms such as viruses and bacteria. Such films are found in various articles including wound coverings, transdermal patches, operating room drapes, protective clothing, diapers, personal hygiene products (feminine hygiene, incontinency), waterproof and outdoor clothing articles, food packaging such as for fresh vegetables, fruit, cheese and meat, films used in plant growing environments and any end-use where it is desirable to combine "breathability" and liquid barrier properties to liquids and microorganisms.
- Films made from the inventive compositions also demonstrate good adhesion to substrates made from materials containing certain functional groups that react with the "reactive groups" described hereinafter. Such substrates include melamine.

Background of the Invention

- Various thermoplastic materials are known for forming films demonstrating both liquid barrier properties and moisture vapor permeability. Included among these are copolyether esters, copolyether amides and polyurethanes. While films of these materials perform well and meet the performance requirements of various end uses, a drawback they possess is their relative high cost in comparison to other thermoplastic materials.
- It is an object of the present invention to provide a new thermoplastic composition and film therefrom possessing desirable performance characteristics at a reduced cost. According to the invention, a thermoplastic composition is provided containing a mixture of (a) a block copolyether ester, a block copolyether amide and/or a polyurethane; (b) a thermoplastic homo- co- or terpolymer that is incompatible with (a); and (c) a compatibilizer.

Component (b) of the composition is a lower cost thermoplastic material which has insufficient moisture vapor permeability to be suitable for the end-uses previously mentioned. It is incompatible with component (a) and, were the two to be combined together and
5 formed into a film, such film would have a profile showing long laminae or sheets of component (b). Accordingly, films made from such a composition would have a permeability restricted by the specific permeability of component (b), and poor mechanical properties, e.g. a tendency to delaminate.

10 According to the present invention, it has been surprisingly found that a compatibilizer can be combined with components (a) and (b) to yield a film having a moisture vapor transmission rate (MVTR) approaching that of the theoretical value calculated as follows:

15
$$\text{MVTR}_{\text{theor}} = (\text{MVTR}_{\text{comp.(a)}})(\text{weight \% comp.(a)}) + (\text{MVTR}_{\text{comp.(b)}})(\text{weight \% comp.(b)}).$$

20 Another unexpected effect of the addition of the compatibilizer is the improved sealability and adhesion of the compatibilized blend to itself and other substrates, such as melamine.

Detailed Description of the Invention

25 As used herein, certain terms are defined as follows.

"Compatibility" of thermoplastic materials is an art-recognized term that refers, generally, to the degree in which the thermoplastic materials are miscible and/or interact with each other. Accordingly,
30 "incompatible", as used herein, means that the components (a) and (b) are substantially immiscible and/or do interact with each other.

"Compatibilizer" means a thermoplastic material which serves to prevent formation of the previously mentioned laminae of
35 component (b) in a film according to the invention. The compatibilizer has a character which makes it simultaneously soluble or reactive with component (a) and interactive with component (b),

thereby reducing the surface energy of component (b) in component (a), leading to the formation of a dispersion of globules of component (b) in the film.

- 5 Block copolyether esters, block copolyether amides and polyurethanes to be used for component (a) are known per se. Preferred block copolyether esters are segmented elastomers having soft polyether segments and hard polyester segments (c.f. U.S. Patent No. 4,739,012), available from the DuPont Company under the name
10 Hytrel®.

Suitable block copolyether amides for use in the invention are available under the name Pebax® from Elf Atochem.

- 15 The amount of component (a) in the composition will vary depending upon the type of component (a), the type of component (b), desired level of moisture vapor permeability and other factors known to one skilled in the art. Component (a) is typically present in the composition according to the invention in an amount ranging from 25
20 to 90 % by weight, more preferably 50 to 80 %.

- Component (b) according to the invention, is, as previously mentioned, substantially incompatible with component (a). Component (b) may be a homopolymer of an alpha-olefin; a co- or
25 terpolymer containing an alpha-olefin and one or more other monomers; or a block copolymer of a vinylarene and a conjugated diene.

- Where component (b) is a homopolymer, it preferably contains the
30 repeating unit $R-CH=CH_2$ in which R is hydrogen or an alkyl radical having between 1 and 8 carbon atoms. Preferred homopolymers according to the invention are polyethylene (low density (PE-LD), linear low density (PE-LLD), high density (HDPE) and very low density (VLDPE)) and polypropylene.

- 35 Where component (b) is a co- or terpolymer, it preferably contains the repeating unit $R-CH=CH_2$ above, with at least one further

monoethylenically unsaturated, such as aliphatic or aromatic, monomer, the following of which can be cited by way of example: vinyl acetate, styrene, and (meth)acrylic derivatives. This other monomer can represent up to 20% by weight of the olefinic copolymer, preferably from 1 to 10% by weight.

- Preferred copolymers to be used as component (b) according to the invention are copolymers of ethylene and propylene, ethylene-vinyl acetate copolymers, copolymers of ethylene and acrylic derivatives (e.g. copolymers of ethylene, carbon monoxide and n-butyl acrylate, commonly known as EnBACO), copolymers of ethylenically unsaturated carboxylic acid monomers (e.g. acrylic acid, methacrylic acid, crotonic acid, etc.) or the neutralized metallic salts thereof (e.g. as found in the partially neutralized ethylene/carboxylic acid copolymers which are commonly referred to in the art as ionomers), terpolymers based on olefin, methyl acrylate and ethyl acrylate or even mixtures of straight-chain and radicalar low density polyolefins.
- Where component (b) is a block copolymer of a vinylarene and a conjugated diene, it may have the general structure A-B-A wherein the two terminal polymer blocks A comprise thermoplastic polymer blocks of vinylarenes such as polystyrene, while block B is a polymer block of selectively hydrogenated conjugated diene such as isoprene or butadiene (cf. U.S. Patent Re. No. 27,145; U.S. Patent No. 4,548,988). The proportion of the thermoplastic terminal blocks to the center elastomeric polymer block and the relative molecular weights of each of these blocks is balanced to obtain a rubber having an optimum combination of properties such that it behaves as a vulcanized rubber without requiring the actual step of vulcanization. Moreover, these block copolymers can be designed not only with this important advantage but also so as to be handled in thermoplastic forming equipment and are soluble in a variety of relatively low cost solvents.
- Optionally, these block copolymers can be grafted with maleic anhydride so as to form adducts which contain 0.1 to 10% by weight, preferably 0.2 to 5%, of maleic anhydride (see U.S. Patent 4,578,429).

Such compounds are commonly referred to as S-EB-S block copolymers and are available from Shell Chemical Company under the name Kraton®.

- 5 Component (b) is typically present in the composition of the instant invention in an amount ranging from 10-70% by weight.

10 The compatibilizer (component (c)) is chosen according to the nature of component (b). It will have a backbone that is compatible with, and is preferably identical to, component (b) and a reactive group which is compatible or interacts with component (a). This changes the morphology of the composition according to the invention such that the component (b) is distributed in component (b) in the form of globules rather than laminae.

15 The reactive group may be a grafting monomer that is grafted to this backbone, and is or contains at least one alpha- or beta-ethylenically unsaturated carboxylic acid or anhydrides, or a derivative thereof. Examples of such carboxylic acids and anhydrides, which may be
20 mono-, di- or polycarboxylic acids, are acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, itaconic anhydride, maleic anhydride and substituted maleic anhydride e.g. dimethyl maleic anhydride. Examples of derivatives of the unsaturated acids are salts, amides, imides and esters e.g. mono- and
25 disodium maleate, acrylamide, maleimide and diethyl fumarate.

Maleic anhydride is a preferred grafting monomer (reactive group).

30 Preferred backbones for component (c) include polyethylene (low density (PE-LD), linear low density (PE-LLD), high density (HDPE) and very low density (VLDPE)) and polypropylene.

35 The grafting of the polymers can be carried out in the melt state, in solution or in suspension as described. The melt viscosity of the grafted polymer is not restricted, however, most effective alloying is found if the melt index, measured at 2.16 kg and 190°C is between 1

and 150 g/cm³. Such grafted polymers can be prepared as known in the art (cf. European Patent Application 370 735 and 370 736).

5 The compatibilizer is typically present in the composition of the instant invention in a an amount ranging from 0.1 to 15% by weight, preferably between 0.1 and 3%.

10 In addition to the above components, compositions according to the invention may contain conventional additives, such as melt flow modifying agents (e.g. calcium carbonate, silicas, clay, talc) and stabilizers, such as antioxidants and ultraviolet absorbers. The properties these additives bring to the composition and the amounts in which they can be used are known to the skilled artisan.

15 The compositions according to the invention can be prepared according to methods and techniques known in the art, e.g. by (physical) tumble blending.

20 A suitable compounding technique is as follows: a polyether ester and polyethylene are compounded in a Berstorff 25 mm twin screw extruder at a temperature ranging from 200-240 °C. Strands of copolymer so produced are water cooled and granulated.

25 The compositions are made into films using blown film processing. For example, granules produced as above are fed into an extruder having a length/diameter ratio of 27-28, a mixing head and 3-zone screw and equipped with a spiral die and a blown film unit. Films so produced have a thickness of about 50 microns.

30 Examples

Physical blends and compounded blends are prepared having the compositions indicated in Table 1 below. Films having a thickness of 25 µm are extruded and moisture vapor transmission rate (MTVR) is measured according to ASTM E 96 BW.

35

Polymer A = a block polyether ester segmented elastomer containing about, by weight, 31% dimethyl terephthalate, 9% dimethyl isophthalate, 55% ethylene oxide end-capped polypropylene glycol and 16% butane diol; melt flow index (MFI) = 10 dg/min at 190 °C under 2.16 kg according to ASTM D 1238).

Polymer B = Stamylan[®] 2304 (available from DSM; a low density polyethylene, density of 0.92 kg/m³, MFI = 4.4 dg/min (ASTM D 1238)).

Polymer C = Fusabond[®] EMB 226 D (available from the DuPont Company; backbone of PE-LLD, density of 0.92 kg/m³, MFI = 4.4 dg/min (ASTM D 1238), comonomer content: 7% butene, maleic anhydride content: 1%).

Table 1

	Control 1	Control 2	Control 3	Example 1	Example 2
Polymer A (parts	100		70	65.8	65.8
Polymer B by		100	30	28.2	28.2
Polymer C weight)				6	6
Blend type	-	-	physical	physical	compound
25 MTR (g/m ² ·day)	2025	9	253	735	657


Films according to the invention demonstrate improved performance properties, such as improved seal strength. This can be demonstrated by sealing the film using a Kopp sealing machine with two sealing bars; dwell time 1 sec, pressure 0.3 MPa; and testing the seal on a Zwick tensile testing machine with 100 mm/min. cross head speed.

Claims:

1. A thermoplastic composition comprising
 - 5 (a) a block copolyether ester, a block copolyether amide, and/or a polyurethane;
 - (b) a thermoplastic homo- co- or terpolymer that is incompatible with (a); and
 - 10 (c) a compatibilizer.
2. A composition according to claim 1 wherein (b) is a homopolymer of an alpha-olefin; a co- or terpolymer containing an alpha-olefin and one or more other monomers; or a block
15 copolymer of a vinylarene and a conjugated diene.
3. A composition according to claim 2 wherein (c) is a homo- co- or terpolymer whose backbone corresponds to (b) and which is grafted with a monomer having a functional group that is compatible with (a).
20
4. A composition according to claim 1 wherein (a) is a block copolyether ester, (b) is polyethylene, and (c) is a grafted polymer having a backbone of polyethylene that is grafted with maleic anhydride.
25
5. A composition according to claim 1 comprising, by weight, 25 to 90 % (a), 10 to 70% (b) and 0.1 to 15% (c).
6. A film formable from the composition of claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/14365

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : C08L 67/02, 77/00, 75/04, 23/06, 23/08, 71/00 US CL : 525/64, 66, 166, 179 According to International Patent Classification (IPC) or to both national classification and IPC																				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 525/64, 66, 166, 179 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS search terms: hytrel, polyether amide, polyethylene, maleic anhydride																				
C. DOCUMENTS CONSIDERED TO BE RELEVANT																				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																		
X	US, A, 4,368,295 (NEWTON ET AL) 11 January 1983, Abstract, col. 1, line 63 to col. 2, line 6.	1-6																		
Y	JP, A, 59-221353 (MITSUI PETROCHEM IND KK) 12 December 1984, Abstract.	1-6																		
Y	JP, A, 60-58447 (MITSUI PETROCHEM IND KK) 04 April 1985, Abstract.	1-6																		
A	JP, A, 56-100846 (MITSUBISHI CHEM IND KK) 13 August 1981, Abstract.	1-6																		
Y	US, A, 4,739,012 (HAGMAN) 19 April 1988, col.4, line 14 to col. 6, line 51.	1-6																		
Y	US, A, 3,023,192 (SHIVERS, JR. ET AL) 27 February 1962, entire document.	1-6																		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.																				
<table border="0"> <tr> <td>* Special categories of cited documents:</td> <td>* T</td> <td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>* A* document defining the general state of the art which is not considered to be part of particular relevance</td> <td>* X*</td> <td>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>* E* earlier document published on or after the international filing date</td> <td>* Y*</td> <td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>* L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>* &*</td> <td>document member of the same patent family</td> </tr> <tr> <td>* O* document referring to an oral disclosure, use, exhibition or other means</td> <td></td> <td></td> </tr> <tr> <td>* P* document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table>			* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	* A* document defining the general state of the art which is not considered to be part of particular relevance	* X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	* E* earlier document published on or after the international filing date	* Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	* L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* &*	document member of the same patent family	* O* document referring to an oral disclosure, use, exhibition or other means			* P* document published prior to the international filing date but later than the priority date claimed		
* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention																		
* A* document defining the general state of the art which is not considered to be part of particular relevance	* X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone																		
* E* earlier document published on or after the international filing date	* Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																		
* L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* &*	document member of the same patent family																		
* O* document referring to an oral disclosure, use, exhibition or other means																				
* P* document published prior to the international filing date but later than the priority date claimed																				
Date of the actual completion of the international search 01 MARCH 1995		Date of mailing of the international search report 31 MAR 1995																		
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer  IRINA S. ZEMEL Telephone No. (703) 308-2351																		